Phase diagram of iron, revised-core temperatures

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[1] Shock-wave experiments on iron preheated to 1573 K from 14 to 73 GPa, yield sound velocities of the γ- and liquid-phases. Melting is observed in the highest pressure (∼71 ± 2 GPa) experiments at calculated shock temperatures of 2775 ± 160 K. This single crossing of the γ-liquid boundary agrees with the γ-iron melting line of *Boehler* [1993], *Saxena et al.* [1993], and *Jephcoat and Besedin* [1997]. This γ-iron melting curve is ∼300°C lower than that of *Shen et al.* [1998] at 80 GPa. In agreement with *Brown* [2001] the discrepancy between the diamond cell melting data and the iron shock temperatures require the occurrence of yet another sub-solidus phase along the principal Hugoniot at ∼200 GPa. This would reconcile the static and dynamic data for iron's melting curve. Upward pressure and temperature extrapolation of the γ-iron melting curve to 330 GPa yields 5300 ± 400 K for the inner core-outer core boundary temperature. *INDEX TERMS:* 8124 Tectonophysics: Earth's interior—composition and state; 3919 Mineral Physics: Equations of state; 3924 Mineral Physics: High-pressure behavior; 3944 Mineral Physics: Shock wave experiments

1. Introduction

[2] The melting temperature of iron under high pressures is a critical constraint to the temperature in the Earth's interior. The pressure and temperature state existing at the outer-core, inner-core (OC-IC) boundary should also lie on the melting curve of molten iron alloy. Considerable uncertainty has existed regarding the phase diagram of iron and, especially, its melting curve [*Boehler*, 1993; *Brown and McQueen*, 1986; *Saxena et al.*, 1994; *Shen et al.*, 1998; *Williams et al.*, 1991]. We report the first measurements of sound velocity in iron under high pressures (15–73 GPa) at initial temperature of 1573 ± 50 K within the γ stability field by shock-wave experiments. This study independently tests previous discrepant melting data of γ-iron data [*Boehler*, 1993; *Saxena et al.*, 1994; *Shen et al.*, 1998; *Williams et al.*, 1991] in this pressure range.

2. Experimental Methods and Results

[3] The experiments are of two types (see *Chen and Ahrens* [1998a; 1998b]) for details). (a) Equation-of-state (EOS) experiments (described first) and (b) sound velocity behind the shock front.

[4] (a) The equation-of-state experiments employed heating techniques derived from our previous high-temperature shock wave investigations.

[5] Several improvements over the methods previously employed by our group are described in detail in *Chen and Ahrens* [1998b].

[6] We used polycrystalline iron (99%) targets in the shape of two cylinders with diameters of 13 and 38 mm, and heights, 4 and 2 mm. Sample temperature (±2°), was monitored with a two-color infrared pyrometer (Williamson 8120S-C-WD2). The initial density of the sample is determined from the measured temperature.

[7] The variation in the target temperature along the center line was calculated to vary by a maximum value of ∼52 K. (The surface toward R-F coil is hotter).

[8] Using copper 3-, rather than 6-mm, O.D. tubing for r-f heating, we measured a variation in temperature of ∼40 K along the sample radius of the 13 mm upper diameter of the Mo container encapsulating the iron sample.

[9] We note that for the VISAR shots, the iron sample is covered with a 0.5 mm thick shim of polycrystalline Mo.

[10] For γ-iron (at 1573 K) an initial density is 7.413 ± 0.012 Mg/m^3, we fired seven impact EOS experiments. These closely define the Hugoniot curve in the shock velocity, U_s, particle velocity, u_p, plane as

$$U_s = 4.102(0.013)\text{km/s} + 1.610(0.014)u_p. \tag{1}$$

over the range of 17 to 74 GPa. Using the *Ruoff* [1967] relations, an isentropic bulk modulus K_s of 124.7 (1.1) GPa and pressure derivative of the isentropic modulus of 5.44 (0.06) was obtained. The high-temperature equation-of-state is given in detail in *Chen and Ahrens* [1998a].

[11] (b) The VISAR (Velocity Interferometer System for Any Reflector) method, can be applied to measuring free-surface velocity histories and hence sound velocity at high pressures and temperatures in the compressed material behind the shock front (see *Duffy and Ahrens* [1994]).

3. Results

[12] The free-surface velocity history is measured at single (central) location in the target. This method is different than the experimental method of *Brown and McQueen* [1986].

[13] In both the methods the velocity of the initial rarefaction wave at the peak shock pressure is measured. For molten and solid material, the initial unloading wave velocities are:

$$V_b = [K_s/\rho]^{1/2} \tag{2a}$$

$$V_p = \left[\left(K_s + \frac{4}{3}\mu\right)/\rho\right]^{1/2} \tag{2b}$$

where μ is shear modulus. At low pressure, γ-iron initially unloads with P-wave velocity (2b). For shock pressures greater than ∼71 GPa the unloading velocity is V_b (2a) as is expected for molten Fe.

[14] The initial release wave velocity data (Table 1) in the sample (Lagrangian) reference frame and previous measurements are shown in Figure 1. Our data for γ-iron indicate a sharp drop in

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Table 1. Longitudinal Velocity along the Hugoniot for γ- iron, Initially at 1573 K, Driven to States in the γ-, γ- and Liquid-iron Regimes

Shot	Pressure (GPa)	Density (Mg/m^3)	Vp (Fe) (km/s)	Calculated Shock Temperature (K)	Phase
1014	15.2	8.13	6.08	1848 (65)	γ
961[a]	17.4	8.23	>5.69	1883 (69)	γ
1013	25.6	8.51	6.12	2012 (81)	γ
1007	54.8	9.29	7.31	2455 (176)	γ
1010	69.6	9.58	7.74	2767 (161)	γ
1008	71.6	9.62	6.55	2780 (161)	γ + liquid
1011	72.1	9.63	7.22	2795 (161)	γ + liquid
1015	72.4	9.64	6.80	2812 (161)	γ + liquid

[a] Point not plotted in Figure 1.

sound velocity at ∼71 GPa along its Hugoniot centered at 1573 K. The 72 GPa (Shot 1008) datum agrees well with liquid iron curve interpolated between Brown and McQueen's shock-wave data and *Nasch et al.*'s [1994] ultrasonic data. Therefore, we infer the steep drop in sound velocity at 71 ± 2 GPa corresponds to the melting of γ-iron along the γ-Hugoniot centered at 1573 K.

4. Discussion

[15] *Boehler and Ross* [1997] (B&R) suggested the onset of melting occurs at 200 GPa, along the principal iron Hugoniot. They suggest that the 0.5 km/sec decrease in sound velocity that begins at 200 GPa is too large for a polymorphic phase change and at 234 GPa, shock melting is complete.

[16] To evaluate the B&R hypothesis we examine data for other substances. We sought an example for which the close alignment of 4 data points such as in the 205 to 234 GPa range is accidental and does not define a phase change. No such example in the previous sound velocity along the Hugoniot literature was found. Moreover, the B&R 10% characteristic velocity decrease in going from Eq 2b to Eq 2a, for melting is not all that characteristic. The P-wave velocity decreases observed upon melting are quite variable. For 316 stainless steel [*Hixson et al.*, 1994] and Ta [*Brown and Shaner*, 1984] these are 3 and 11%; whereas 2024Al gives a decrease of ∼18% upon melting [*Shaner*, 1981]!

[17] The present γ-iron sound velocity data lie slightly above the extrapolation of Brown and McQueen's purported γ-iron data (the middle dashed line in Figure 1). As the elastic velocity usually decreases with increasing temperature, their data appears to correspond to much higher temperatures. However, other evidence that *Brown and McQueen* [1986] sampled a phase, other than γ-iron in the 210 to 234 GPa range, is discussed below. We believe V_p

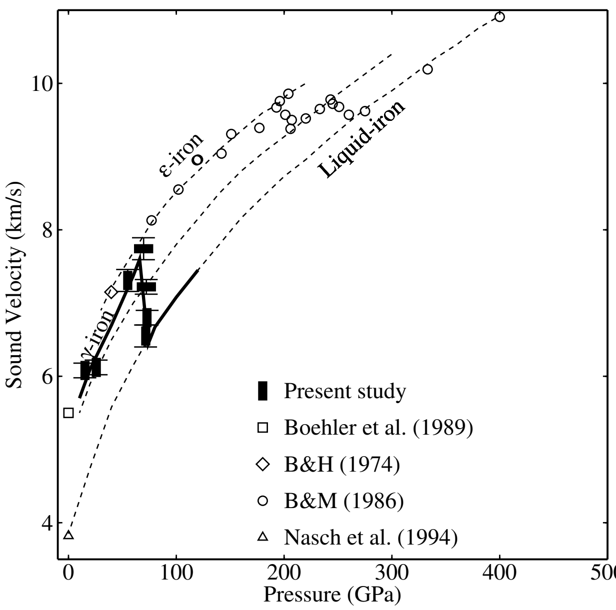

Figure 1. Sound velocity measurements. Present data indicate γ-iron melts at 71 ± 2 GPa. Note that γ-iron appears to lie on a distinctively higher P-wave velocity versus pressure curve through the data measured by *Brown and McQueen* [1986] that lie ∼5% lower. We believe that this velocity as measured in the 210 GPa to 243 GPa range may represent β-iron phase. Abbreviations: B & H: *Barker and Hollenbach* [1974]; B & M: *Brown and McQueen* [1986] (modified from *Chen and Ahrens* [1998a]).

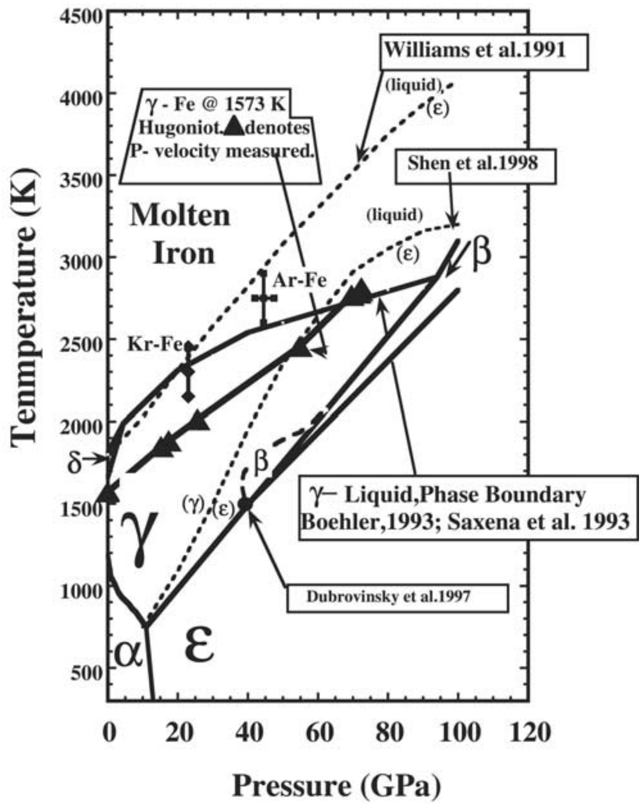

Figure 2. Calculated shock temperature versus pressure for 1573 K shock-wave experiments on iron. Phase diagram from *Boehler* [1993], *Saxena et al.* [1993], *Dubrovinsky et al.* [1997], and *Shen et al.* [1998]. Also, shown are data where the melting curve of Fe crosses high-pressure melting curves of Ar and Kr (*Jephcoat and Besedin* [1997]). These data also support the present results, but are also several hundred degrees below those of *Williams et al.* [1991].

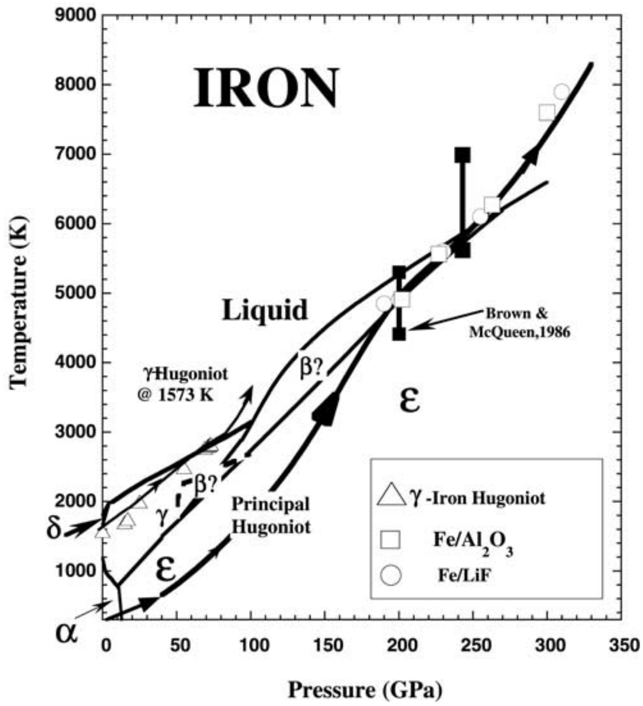

Figure 3. Proposed phase diagram of iron. The 1573 K γ-phase values of the Hugoniot sound speed are consistent with phase diagrams of *Boehler* [1993] and *Saxena et al.* [1993]. The principal Hugoniot appears to cross the ε-(?) phase boundary at 200 GPa, and the (?)-liquid phase boundary at 243 GPa as proposed by *Brown* [2001]. *Holland*'s [1999] revised shock temperatures taken with LiF and Al_2O_3 anvils are shown relative to Brown and McQueen's calculated shock temperatures (from *Holland* [1999]).

between 15.2 and 69.6 GPa along the 1573K Hugoniot is for γ-iron because:

1. The data begins in the γ-iron field. The low-pressure portion of the phase diagram is better determined.

2. We calculate V_p for γ-iron at ambient pressure as 5.3 km/s from static compression data [*Boehler et al.*, 1989]. This compares to our low pressure V_p datum of 6.08 km/s at 15.2 GPa. From this we estimate

$$\left(\frac{\partial V_p}{\partial P}\right)_S = 5.13 \times 10^{-2}(\text{km/s/GPa}) \qquad (3)$$

for γ-iron at 1573 K.

3. The origin of the 200 GPa decrease in Brown and McQueen's V_p data [*Belonoshko*, 1997; *Boehler*, 1993] has not been clear. *Nguyen and Holmes* [2000] report only a single drop in sound velocity along the iron principal Hugoniot between 220 and 250 GPa which they attribute to melting. The present γ-iron V_p data (Table 1) are 0.25 to 0.4 km/sec higher than inferred upon downward extrapolation of the Brown & McQueen result. We infer from Figure 1 that the decrease of ~0.5 km/sec in V_p at 200 GPa is probably not due to the ε- to γ-phase transition, but rather, represents another solid-solid phase change (as recently suggested by *Brown* [2001]) possibly to the dhcp (β) phase as suggested by *Boehler* [1993] and *Saxena et al.* [1996], see Figure 2.

[18] The γ-shock temperatures of Figure 2 have uncertainties of ±65 K at 15.2 GPa to ±161 K at 72.4 GPa, arising from uncertainties of specific heat. The Grüneisen parameter is determined from the bulk sound velocity. Gamma-iron does not appear to demonstrate major super-heating behavior prior to shock melting. This is in agreement with *Holland*'s [1999] results (Figure 3). A small thermal overshoot upon melting as suggested by *Yoo et al.* [1993] can, however, not be ruled out.

[19] Because our γ-Hugoniot would intersect the γ-ε phase line proposed by *Shen et al.* [1998] at approximately 50 GPa and 2400 K, we would expect the 54.8 GPa datum (shot 1007, Table 1) to have a sound velocity value characteristic of the ε phase (7.6 km/sec) and not the observed 7.3 km/sec. Moreover, the sharp drop in sound velocity at 71 ± 2 GPa is not predicted by the *Shen et al.* [1998] phase diagram. The Shen et al. phase diagram has transformation from γ- to ε-phase occurring at ~55 GPa and melting of the ε phase at ~85 GPa. Moreover, Shen et al. conducted in-situ energy dispersion analysis and did not observe the β (dhcp) structure found by several authors (e.g. *Andrault et al.* [1997]). S. Saxena (private communication) indicates that he does not expect the ε- to β-transition to be detectable with the usual energy dispersive system. In contrast, a phase change related to the increase in V_p between Hugoniot states at 54.8 to 70 GPa, over that expected on the basis of increased compression alone, is not observed. Finally, melting of the γ-phase is inferred to occur at 71 ± 2 GPa on the basis of a 12% decrease in V_p.

5. Application to the Core

[20] Our main result is that γ-iron shocked from an initial temperature of 1573 K, enters the liquid field at 71 ± 2 GPa and ~2775 K. This supports the phase diagrams proposed by *Boehler* [1993] and *Saxena et al.* [1996].

[21] The present value of V_b = 6.55 km/sec for molten iron yields a value of Grüneisen parameter $\gamma = 1.63 \pm 0.28$ at $\rho = 9.62 \pm 0.02$ Mg/m^3 using the equations 2–7 of *Brown and McQueen* [1986].

[22] The molten iron γ value is close to what is expected interpolating between 7.00 Mg/m^3 and Brown and McQueen result of $\gamma = 1.35$ at a density of 12.6 Mg/m^3. The present result also agrees with the zero-pressure value of 1.7 for molten iron upon plotting γ versus density (Chen et al. [1998a] and *Hixson et al.*'s [1990]) molten iron data between 5.5 and 6.5 Mg/m^3.

[23] Using the present Grüneisen parameter for γ-iron (1.67), we apply the Lindemann relation to extrapolate the melting datum to higher pressures.

[24] At the pressure of the outer-inner core boundary the γ-iron melting point (330 GPa) is 5300 ± 400 K. To obtain this result we integrate Eq. 13 [*Brown and McQueen*, 1986] from T_m = 2775 K and 72 GPa to T_m at 330 GPa, using a constant value of $\gamma\rho$ = 16.08. Like *Boehler*'s [1993] calculations based on the melting of γ-iron at high-pressure, this calculation suggests that the IC-OC temperature (and the core side of the CMB) are at lower temperatures than those those inferred from shock temperature measurements above 200 GPa of 7600 K and 6830 K [*Williams et al.*, 1987; *Yoo et al.*, 1993]. This assumes no eutectic lowering of the iron melting point following the results of *Boehler* [1996]. The temperature on the outer core side of the CMB must be higher than the melting temperature at 136 GPa, i.e., which we estimate at 3400 ± 200 K from the Lindemann relation. Again using the Grüneisen parameter data for iron, another estimate can be obtained by isentropically decompressing liquid iron alloy from its melting point at the ICB to the CMB using the above values of the Grüneisen parameter for liquid iron. The temperature of the core side of the CMB temperature is 3660 ± 600 K (implying, since this is greater than the 136 GPa melting point of γ-iron of 3400 ± 200 K, that the core remains molten).

[25] Estimates of the lowermost mantle, T_{CMB}, range from 2550 to 2750 K [*Boehler*, 1982; *Jeanloz and Morris*, 1986; *Shankland and Brown*, 1985]. From T_{CMB} and our estimate of the outermost core temperature, we find a lowermost mantle thermal boundary layer temperature difference that is only weakly constrained and could range from 300 to 1400 C.

[26] The phase diagram inferred from *Holland and Ahrens* [1997] shock data shown in Figure 3 has a melting point of 6700 K at 330 GPa that is much higher than the 5300 K that results from extrapolating the γ-iron-melting data. Both Figure 3 and the recent analyses of *Brown* [2001] suggest, in contrast to the conclusion of *Nguyen and Holmes* [2000], the shock states achieved upon melting iron along its principal Hugoniot may well reflect the melting of another high-pressure phase of iron, that is not ε-iron.

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References

Andrault, D., et al., The orthorhombic structure of iron: An in-situ study at high-temperature and high-pressure, *Science*, *278*, 831–834, 1997.

Barker, L. M., and R. E. Hollenbach, Shock wave study of the α–ε transition in iron, *J. Appl. Phys.*, *45*, 4872–4887, 1974.

Belonoshko, A. B., Atomic simulation of shock wave-induced melting in argon, *Science*, *275*, 955–957, 1997.

Boehler, R., Adiabats of quartz, coesite, olivine, and magnesium-oxide to 50 kbar and 1000 K and the adiabatic gradient in the Earth's mantle, *J. Geophys. Res.*, *87*, 5501–5506, 1982.

Boehler, R., Temperatures in the Earth's core from melting-point measurements of iron at high pressures, *Nature*, *363*, 534–536, 1993.

Boehler, R., Melting temperature of the Earth's mantle and core: Earth's thermal structure, *Ann. Rev. Earth Planet. Sci.*, *24*, 15–40, 1996.

Boehler, R., et al., X-ray diffraction of γ-iron at high temperatures and pressures, *J. Appl. Phys.*, *65*, 1795–1797, 1989.

Boehler, R., and M. Ross, Melting curve of aluminum in a diamond cell to 0.8 Mbu implications for iron, *Ann. Rev. Earth Planet. Sci. Lett.*, *153*, 223–227, 1997.

Brown, J. M., The equation of state of iron to 450 GPa: Another high pressure solid phase?, *Geophys. Res. Lett.*, *28*, 4339–4342, 2001.

Brown, J. M., and R. G. McQueen, Phase transitions, Grüneisen parameter, and elasticity for shocked iron between 77 GPa and 400 GPa, *J. Geophys. Res.*, *91*, 7485–7494, 1986.

Brown, J. M., and J. W. Shaner, Rarefaction velocities in shocked tantalum and the high pressure melting point, in *Shock Waves in Condensed Matte—1983*, edited by J. R. Asay, R. A. Graham, and G. K. Straub, pp. 91–94, Elsevier, New York, 1984.

Chen, G. Q., and T. J. Ahrens, High pressure and high temperature equation-of-state of gamma and liquid iron, in *High-Pressure Materials Research*, vol. 499, edited by R. M. Wentzcovitch, R. J. Hemley, W. J. Nellis, and P. Y. Yu, pp. 41–61, Mat. Res. Soc. Symp. Proc., Warrendale, PA, 1998a.

Chen, G. Q., and T. J. Ahrens, Radio frequency heating coils for shock wave experiments, in *High-Pressure Materials Research*, vol. 499, edited by R. M. Wentzcovitch, R. J. Hemley, W. J. Nellis, and P. Y. Yu, pp. 63–71, Mat. Res. Soc. Symp. Proc., Warrendale, PA, 1998b.

Dubrovinsky, L. S., S. K. Saxena, and P. Lazor, X-ray study of iron with heating at ultra-high pressure, *Geophys. Res. Lett.*, *24*, 1835–1838, 1997.

Duffy, T. S., and T. J. Ahrens, Dynamic response of molybdenum shock compressed at 1400^3C, *J. Appl. Phys.*, *76*, 835–842, 1994.

Hixson, R. S., R. G. McQueen, and J. N. Fritz, The shock Hugoniot of 316 SS and sound velocity measurements, in *High Pressure Science and Technology—1993*, edited by S. C. Schmidt, J. W. Shaner, G. A. Samara, and M. Ross, pp. 105–108, Amer. Inst. Phys., New York, 1994.

Hixson, R. S., M. A. Winkler, and M. L. Hodgdon, Sound speed and thermophysical properties of iron and nickel, *Phys. Rev. B*, *42*, 6485–6491, 1990.

Holland, K. G., Phase Changes and Transport Properties of Geophysical Materials under Shock Loading, Ph.D. (Major: Geophysics) thesis, 90 pp., Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California, 1999.

Holland, K. G., and T. J. Ahrens, Melting of $(Mg,Fe)_2SiO_4$ and the core-mantle boundary of the Earth, *Science*, *275*, [5306], 1623–1625, 1997.

Jeanloz, R., and S. Morris, Temperature distribution in the crust and mantle, *Ann. Rev. Earth Planet. Sci*, *14*, 377–415, 1986.

Jephcoat, A. P., and S. P. Besedin, Melting of rare-gas solids Ar, Kr, Xe at high pressures and fixed points in the P-T plane, in *Properties of Earth and Planetary Materials*, edited by M. Manghnani and T. Yagi, pp. 287–296, AGU, Wash. D.C., 1997.

Nasch, P. M., M. H. Manghnani, and R. A. Secco, Sound-velocity measurements in liquid-iron by ultrasonic interferometry, *J. Geophys. Res.*, *99*, 4285–4291, 1994.

Nguyen, J. C., and N. C. Holmes, Iron sound velocities in shock wave experiments, in *Shock Compression of Condensed Matter—1999*, vol. AIP Conf. Proc. 505, edited by M. D. Furnish, L. C. Chhabildas, and R. S. Hixon, pp. 81–84, Amer. Inst. Phys., Melville, NY, 2000.

Ruoff, A. L., Linear shock-velocity-particle-velocity relationship, *J. Appl. Phys.*, *38*, 4976–4980, 1967.

Saxena, S. K., L. S. Dubrovinsky, and P. Häggkvist, X-ray evidence for the new phase beta-iron at high-temperature and high-pressure, *Geophys. Res. Lett.*, *23*, 2441–2444, 1996.

Saxena, S. K., G. Shen, and P. Lazor, Experimental evidence for a new iron phase and implications for Earth's core, *Science*, *260*, 1312–1314, 1993.

Saxena, S. K., G. Shen, and P. Lazor, Temperatures in Earth's core based on melting and phase transformation experiments on iron, *Science*, *264*, 405–407, 1994.

Shaner, J. W., New ways of looking for phase transitions at multi-megabar dynamic pressures, in *Physics of Solids Under High Pressure*, edited by J. S. Shilling, and R. Shelton, pp. 99–108, North-Holland, Amsterdam, 1981.

Shankland, T. J., and J. M. Brown, Homogeneity and temperatures in the lower mantle, *Physics of the Earth and Planet. Inter.*, *38*, 51–58, 1985.

Shen, G. Y., et al., Melting and crystal-structure of iron at high pressures and temperatures, *Geophys. Res. Lett.*, *25*, 373–376, 1998.

Williams, Q., et al., The melting curve of iron to 250 Gigapascals: A constraint on the temperature at Earth's center, *Science*, *236*, 181–182, 1987.

Williams, Q., E. Knittle, and R. Jeanloz, The high-pressure melting curve of iron: A technical discussion, *J. Geophys. Res.*, *96*, 2171–2184, 1991.

Yoo, C. S., et al., Shock temperatures and melting of iron at Earth core conditions, *Phys. Rev. Lett.*, *70*, 3931–3934, 1993.

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